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# Robust organocatalysts for the cleavage of vegetable oil derivatives to aldehydes through retro-benzoin condensation

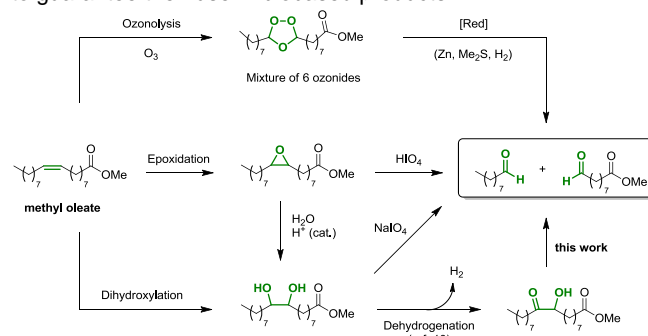
Nam Duc Vu, Souleymane Bah, Elsa Deruer, Nicolas Duguet\* and Marc Lemaire\*

**Abstract:** A series of thiazolium salts was prepared and tested for the cleavage of the  $\alpha$ -hydroxyketone derived from methyl oleate. The robustness of these precatalysts was determined by dynamic thermogravimetric analyses (TGA). It has been shown that the stability of these species is mainly governed by the nature of the counter-anion and some of them were found stable until 350–400°C. The  $\alpha$ -hydroxyketone derived from methyl oleate was cleaved under reactive distillation conditions using optimized, thermally robust *N*-butylthiazolium triflate to give the cleavage product, namely, nonanal and methyl azelaaldehyde, with 85 and 70% yields. A range of  $\alpha$ -hydroxyketones derived from several fatty acids was cleaved to give the corresponding bio-based aldehydes with up to 98% isolated yields. Finally, this protocol was successfully applied to a high-oleic sunflower oil derivative.

## Introduction

Vegetable oils and animal fats (triglycerides) are attractive renewable raw materials for the chemical industry.<sup>[1]</sup> Indeed, their competitive cost and wide availability (about 202 million tons in 2015)<sup>[2]</sup> make them adequate for numerous high-volume commercial applications. For instance, they can be used as biofuel<sup>[3]</sup> (biodiesel) but can be best converted to valuable building blocks for applications in pharmaceuticals, cosmetics, paints, coatings, packaging materials, lubricants, surfactants, fine chemicals and polymers.<sup>[4]</sup> Most of the reactions on oleochemicals occur at the fatty acid carboxy group and they are comparatively few examples on the alkyl chain. However, the presence of double bond(s) in unsaturated fatty acid derivatives allows the installation of a range of organic functions<sup>[5]</sup> including aldehyde,<sup>[6]</sup> epoxide,<sup>[7]</sup> diol,<sup>[8]</sup> ketone and diketone,<sup>[9]</sup>  $\alpha$ -hydroxyketone,<sup>[10]</sup> carbonate,<sup>[11]</sup> among others.<sup>[12]</sup> More importantly, cleavage reactions – mainly using methyl oleate as archetype – can give access to building-blocks with higher added-value, essentially for surfactants and polymer applications. In this respect, the formation of fatty mono- and difunctionalized aldehydes is of great interest as they can be

used for a broad variety of transformations. For example, linear aldehydes can be used for the preparation of bio-based surfactants through reductive alkylation of polyols.<sup>[13]</sup> Moreover, functionalized aldehydes can be transformed to monomers for the preparation of polyesters and polyamides through reduction or reductive amination, respectively.<sup>[8]</sup> However, there are not so many methods to produce aldehydes from vegetable oils or fatty acid derivatives. Thermal cracking of methyl ricinoleate obtained from castor oil produces bio-heptanal as a co-product of nylon-11 (Rilsan®) synthesis.<sup>[14]</sup> This route is very specific to ricinoleic derivatives and requires elevated temperature (> 300°C). Cross-metathesis of unsaturated fatty acid derivatives with ethylene (ethenolysis)<sup>[15]</sup> produces terminal alkenes that can be further transformed to the corresponding homologated aldehydes through carbonylation.<sup>[16]</sup> This sequence is very attractive from a green chemistry point of view but implies the use of gases and requires specialized high-pressure equipments. Other reported routes involve the formation of oxidized intermediates that are cleaved to the desired aldehydes (Scheme 1). Reductive ozonolysis of fatty acid derivatives provides aldehydes with excellent atom-economies.<sup>[17]</sup> However, this method requires the use of ozone (O<sub>3</sub>) which is highly toxic and involves the formation of explosive ozonide intermediates. Moreover, the generation of ozone is a highly energy-intensive process, that also constitutes a serious drawback. Alternatively, fatty epoxides or diols, which are also industrially relevant oleochemicals, can be also cleaved to aldehydes but only using HIO<sub>4</sub> or NaIO<sub>4</sub> as stoichiometric oxidants,<sup>[18]</sup> respectively. In this context, new methodologies should be developed to produce fatty aldehydes to guarantee their use in biobased products.



**Scheme 1.** Main routes to fatty aldehydes from methyl oleate.

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Enzymatic catalysis occupies a pivotal place in the utilization of biomass as renewable feedstock as enzymes are inherently involved in both biosynthetic or biodegradation pathways. Most enzymes produce aldehydes in protected or masked forms (carbohydrates) or use them as transient intermediates. One of

these enzymes is the transketolase (TK) (EC 2.2.1.1). This thiamine diphosphate (ThDP)-dependent enzyme is involved in the metabolism of carbohydrates. Indeed, TK catalyzes *in vivo* the formation of D-glyceraldehyde 3-phosphate from D-xylulose 5-phosphate (aldehyde donor) through the transfer of a two-carbon ketol unit (glycolaldehyde) to D-ribose 5-phosphate (aldehyde acceptor) to give D-sedoheptulose.<sup>[19]</sup> However, the synthetic utility of this transformation is limited due to the reversibility of the process. Some strategies have employed hydroxypyruvic acid as the ketol donor to render the transformation irreversible but free aldehydes could not be produced through these methods.<sup>[20]</sup>

The analogous organocatalyzed process, *i.e.* the chemical formation of aldehydes from the corresponding  $\alpha$ -hydroxyketone, is called "retro-benzoin condensation". Contrary to the (asymmetric) benzoin condensation that was extensively studied using cyanides, thiazolium salts and related *N*-Heterocyclic Carbenes (NHCs),<sup>[21]</sup> only little attention has been paid to the opposite process.<sup>[22]</sup> Miyashita *et al.* were the first to synthetically exploit the retro-benzoin condensation for the preparation of ketones from  $\alpha$ -substituted benzoin.<sup>[23]</sup> The reaction was catalysed either by cyanide ion or NHCs. In that case, the equilibrium of the reaction was shifted towards the formation of ketones, probably thanks to their higher stability. More recently, Chi *et al.* have reported a bio-inspired approach for the generation of formaldehyde equivalents from carbohydrates through a retro-benzoin process catalysed by a thiazolium salt.<sup>[24]</sup> The reactive formyl anion equivalent was reacted with enones to give  $\beta$ -formylketones, thus exploiting the irreversible character of the Stetter reaction to shift the equilibrium of the reaction. However, free aldehydes could not be isolated through the use of these two methodologies.

In this context, we have previously reported the cleavage of the  $\alpha$ -hydroxyketone derived from methyl oleate to aldehydes through a retro-benzoin process catalyzed by a thiazolylidene species.<sup>[25]</sup> We have shown that the aldehydes produced are in equilibrium with their corresponding acyloins. The free aldehydes, *i.e.* nonanal and methyl azelaaldehyde, were recovered by reactive distillation under vacuum and were isolated with poor yields.

We now report here an efficient, robust catalytic system based on a thiazolium salt that allows the cleavage of a series of  $\alpha$ -hydroxyketones derived from vegetable oils with high yields.

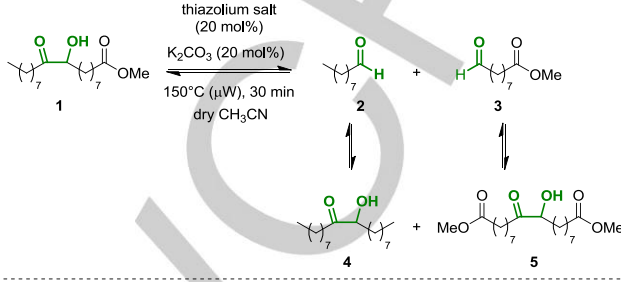
## Results and Discussion

We have previously identified that only thiazolium salts were efficient precatalysts for the cleavage of the  $\alpha$ -hydroxyketone derived from methyl oleate. This observation is in accordance with the work of Chi<sup>[24]</sup> who has also proved the superiority of thiazolium salts (over imidazolium, imidazolinium and triazolium salts) to promote the cleavage of carbohydrate derivatives through a retro-benzoin process.

In the quest for an efficient catalytic system, we have first screened a range of commercially available and structurally diverse thiazolium salts (Table 1). First,  $\alpha$ -hydroxyketone **1** was

treated with thiamine pyrophosphate (ThPP) **6**, thiamine hydrochloride (vitamine B1.HCl) **7.HCl** and thiamine-derived thiazolium salt **8** in the presence of  $K_2CO_3$  at 150°C under microwave irradiation.<sup>[26]</sup>

**Table 1.** Screening of commercially available thiazolium salts.<sup>[a]</sup>



Entry	Thiazolium salt	Conv <sup>[b]</sup> (%)	Yield <sup>[b]</sup> (%)			
			2	3	4	5
1	<b>6</b>	0	0	0	0	0
2 <sup>[c]</sup>	<b>7</b>	0	0	0	0	0
3	<b>8</b>	0	0	0	0	0
4	<b>9</b>	7	7	7	0	0
5	<b>10</b>	26	22	22	4	4
6	<b>11</b>	39	29	29	10	10

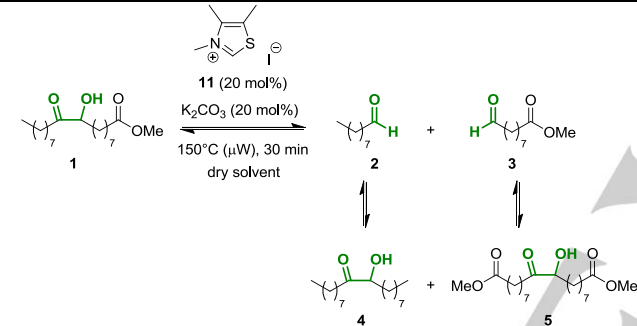
[a] Conditions: Microwave tube,  $\alpha$ -hydroxyketone **1** (1:1 mixture of regioisomers, 0.2 mmol), thiazolium salt (20 mol%),  $K_2CO_3$  (20 mol%), dry  $CH_3CN$  (2 mL), 150°C ( $\mu W$ ), 30 min. [b] Determined by GC using hexadecane as internal standard. [c] 40 mol% of  $K_2CO_3$  were used in this case.

Under these conditions, no conversion of the starting material was observed showing the inability of these catalysts to promote this retro-benzoin process (Table 1, entries 1-3). This could be attributed to the degradation of these catalysts under the reaction conditions. For example, despite that **7** is stable until about 200°C as a salt,<sup>[27]</sup> it could quickly degrade at moderate temperature in organic basic solution.<sup>[28]</sup> With thiamine-derived precatalysts **9** and **10**, the conversion increased from 7% with *N*-ethyl derivative **9** to 26% with precatalyst **10** bearing a *N*-methyl

substituent (Table 1, entries 4-5). These results clearly indicate that the steric bulkiness of the catalyst is deleterious for the activity. Finally, when using less sterically demanding thiazolium **11**, the conversion reached 39% and the aldehydes and their corresponding acyloins were formed with 29 and 10%, respectively (Table 1, entry 6).

A range of various solvents was next tested under standard conditions using thiazolium **11** (20 mol%),  $K_2CO_3$  (20 mol%) at 150°C under microwave irradiation for 30 minutes (Table 2). DMF and EtOAc gave moderate conversion compared to  $CH_3CN$  while non-polar solvents such as toluene and heptane were not found suitable to efficiently promote the reaction (Table 2, entries 1-5). Etheral solvents such as THF, 2Me-THF, MTBE and DBE were also screened but gave poor results (2-6 % conversion) (Table S1 in ESI). Finally, methyl stearate was investigated as bio-based solvent but no conversion was observed under these conditions and  $\alpha$ -hydroxyketone **1** was recovered unaltered (Table 2, entry 6).

**Table 2.** Solvent screening.<sup>[a]</sup>

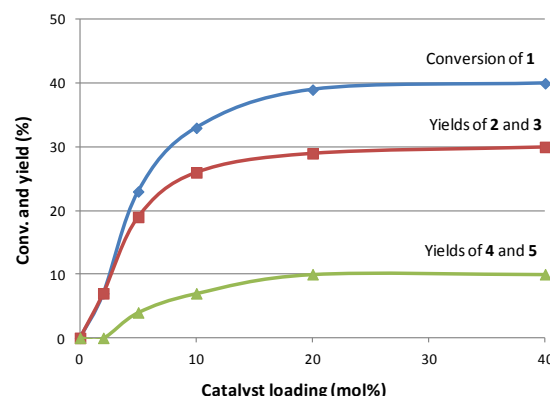


Entry	Solvent	Conv. [b] (%)	Yield <sup>[b]</sup> (%)			
			2	3	4	5
1	$CH_3CN$	39	29	29	10	10
2	DMF	18	13	13	5	5
3	EtOAc	15	13	13	2	2
4	toluene	4	4	4	0	0
5	heptane	3	2	2	1	1
6	methyl stearate	0	0	0	0	0

[a] Conditions: Microwave tube,  $\alpha$ -hydroxyketone **1** (1:1 mixture of regioisomers, 0.2 mmol), thiazolium **11** (20 mol%),  $K_2CO_3$  (20 mol%), dry solvent (2 mL), 150°C ( $\mu W$ ), 30 min. [b] Determined by GC using hexadecane as internal standard. THF = tetrahydrofuran, 2Me-THF = 2-methyl tetrahydrofuran, MTBE = methyl *tert*-butylether, DBE = dibutylether, DMF = dimethylformamide.

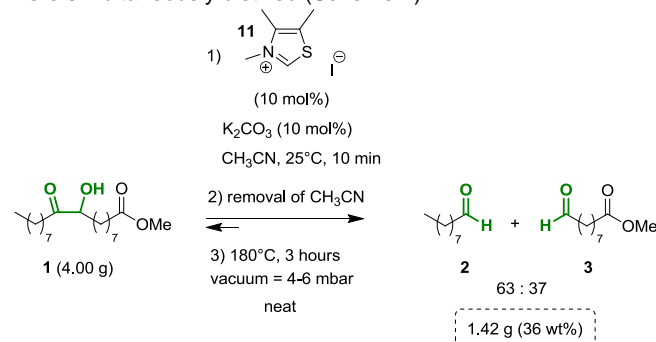
The catalyst loading was next probed at 150°C using optimal thiazolium salt **11** (Figure 1). Expectedly, when increasing the loadings of both the thiazolium salt and the base from 2 to 20%, the conversion increased from 7 to 39% and the yields of the desired aldehydes improved to 29 % (Table S2 in ESI). These

results could not be significantly improved using 40 mol%, indicating that a plateau is reached (Figure 1).



**Figure 1.** Influence of catalyst loading on conversion and yields. Reaction conditions: Microwave tube,  $\alpha$ -hydroxyketone **1** (1:1 mixture of regioisomers, 0.2 mmol), thiazolium **11**,  $K_2CO_3$ , dry  $CH_3CN$  (2 mL), 150°C ( $\mu W$ ), 30 min. The conversion of **1** (blue diamonds), yields of aldehydes **2** and **3** (red squares) and yields of  $\alpha$ -hydroxyketones **4** and **5** (green triangles) were determined by GC using hexadecane as internal standard.

Nevertheless, at 170°C, the conversion reached 56% after 30 minutes and was further improved to 60% after 1 hour. Under these conditions, aldehydes **2-3** and acyloins **4-5** were formed with 40% and 20% yields, respectively (Table S2 in ESI). However, the synthetic utility of this methodology is limited due to the fact that the whole system is in equilibrium. That is the reason why, the cleavage of  $\alpha$ -hydroxyketone **1** was carried out by reactive distillation in order to shift the equilibrium towards the formation of aldehydes **2** and **3**. This strategy should also prevent the formation of symmetrical acyloins **4** and **5**. Thus, thiazolium salt **11** (10 mol%) was treated with  $K_2CO_3$  (10 mol%) in  $CH_3CN$  for 10 min at 25°C. The resulting solution was transferred to a distillation flask containing the starting material and  $CH_3CN$  was removed *in vacuo*. Then, neat  $\alpha$ -hydroxyketone **1** (4.00 g) was heated at 180°C (oil bath) and the aldehydes were simultaneously distilled (Scheme 2).



**Scheme 2.** Recovery of aldehydes by reactive distillation.

The distillation stopped after 3 hours and aldehydes **2-3** were recovered with 36 wt% combined yield as a 63:37 ratio

(Figure 2). Satisfyingly, the residue showed no significant sign of degradation and starting material **1** and acyloin **5** were recovered with 64 wt% combined yield as a 95:5 GC ratio (see Figure S1 in ESI).

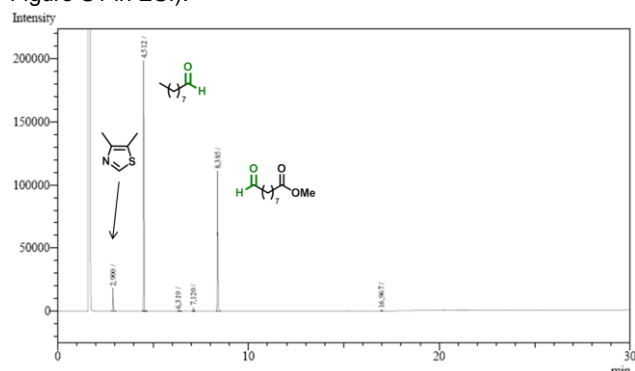
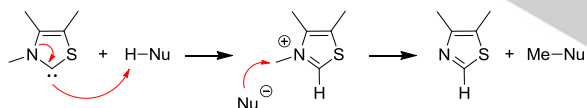


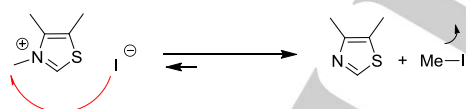
Figure 2. GC chromatogram of the distillate.

These results were encouraging but the yield of aldehydes could not be improved after a prolonged time. We hypothesized that the catalyst has been deactivated or degraded during the reactive distillation under these conditions. This hypothesis has been confirmed by the presence of 4,5-dimethylthiazole – a catalyst fragment – on the GC chromatogram of the distillate (peak at 2.90 min, Figure 2). We proposed a catalyst degradation pathway to account for the formation of this catalyst byproduct. On the one hand, the active thiazolylidene species could be protonated (e.g. by the OH group of the  $\alpha$ -hydroxyketone) and the released nucleophile could react with the activated *N*-methyl group to give 4,5-dimethylthiazole (Scheme 3, a).

a: degradation from the thiazolylidene species



b: degradation from the thiazolium pre-catalyst



Scheme 3. Proposed catalyst degradation pathway.

On the other hand, the degradation could directly occur from the thiazolium iodide, that could be still present in the reaction mixture due to incomplete deprotonation. In that case, the iodide ion could attack the activated *N*-methyl group to cleave the C-N bond leading to 4,5-dimethylthiazole and iodomethane (Scheme 3, b). This degradation pathway, known as the reverse Menshutkin reaction, is quite well established for imidazolium halide salts.<sup>[29]</sup> In our case, the degradation process is accelerated under vacuum since iodomethane is volatile and its

elimination shifts the equilibrium of the reaction.<sup>[30]</sup> For further optimization, the preliminary deprotonation will be avoided as it usually shortens the life time of the catalyst and the thiazolium salt will be used as a reservoir for the thiazolylidene active species.

Structural modifications of the initial precatalyst have been made in order to increase its stability. Two strategies have been envisioned: i) to increase the length or the bulkiness of the *N*-alkyl group, ii) to reduce the nucleophilicity of the counter-ion. The thiazolium salts were prepared either from 4,5-dimethylthiazole by direct alkylation with a range of alkyl halide (I, Br) or pseudohalide (OTf) or from thiazolium iodide **11** by anion metathesis using silver or lithium salts of charge-delocalized soft anions (see ESI). All the thiazolium salts **11–24** prepared in this study are presented in Figure 3.

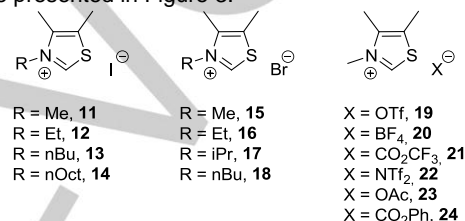


Figure 3. Thiazolium salts used as precatalysts in this study.

It should be noted that thiazolium acetate **23** was specifically prepared in order to install a basic counter-ion that could prevent the use of external base for the generation of the free carbene. However, even if this compound has been characterized by <sup>1</sup>H NMR (see ESI), the product degrades quickly at room temperature. The thermal decomposition of imidazolium carboxylates has already been reported but these species were found stable until 100–200°C.<sup>[31]</sup> The fact that thiazolium acetate **23** readily degrades at room temperature has been attributed to the fact that thiazolium protons are more acidic than their imidazolium counterparts. As a result, the acetate anion has been replaced by a benzoate anion and the corresponding thiazolium benzoate **24** was prepared. Interestingly, the salt crystallizes with one molecule of benzoic acid and the structure has been confirmed by single-crystal X-ray diffraction (Figure 4 and Figure S2 in ESI).

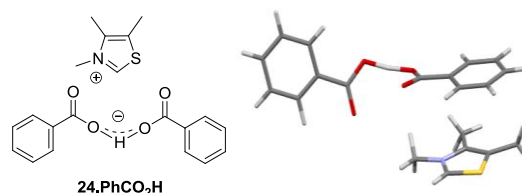


Figure 4. X-ray diffraction of thiazolium benzoate **24·PhCO<sub>2</sub>H**.

The activity of the synthesized thiazolium salts has been evaluated in the retro-Benzoin condensation of the  $\alpha$ -hydroxyketone **1**. The influence of the alkyl chain length was first probed using a range of thiazolium iodides (Table 3).

**Table 3.** Catalytic tests using thiazolium iodides.<sup>[a]</sup>

Reaction scheme for Table 3: A polymer chain with a repeating unit of 7 units is shown. The chain has a carbonyl group (C=O) and a hydroxyl group (OH) on the 7th unit, and a methoxy group (OMe) on the 7th unit. The reaction conditions are:  $K_2CO_3$  (20 mol%),  $CH_3CN$ ,  $150^\circ C$  ( $\mu W$ ), 30 min. The reagent is a thiazolium salt ( $R-N^+(CH_3)S-X$ , 20 mol%). The products are: 2 (aldehyde), 3 (acyl), 4 (aldehyde), and 5 (acyl).

Entry	Thiazolium salts		Conv. <sup>[b]</sup> (%)	Yield <sup>[b]</sup> (%)			
	R	X		2	3	4	5

1	Me	I	11	45	23	23	11	11
2	Et	I	12	25	20	18	4	4
3	<i>n</i> -Bu	I	13	25	16	16	0	0
4	<i>n</i> -Oct	I	14	-	17	17	0	0
5	Et	Br	16	24	18	16	4	4
6	<i>i</i> -Pr	Br	17	3	2	1	0	0

[a] conditions: microwave tube, α-hydroxyketone **1** (1:1 mixture of regioisomers, 0.2 mmol), thiazolium salts (0.04 mmol), K<sub>2</sub>CO<sub>3</sub> (0.04 mmol), dry MeCN (2 mL), 150 °C, 30 min. [b] Yields were determined by GC using *n*-hexadecane as internal standard.

The increase of the alkyl chain length led to a drop of conversion from 45% with *N*-methyl substituent to 17% with *N*-octyl (Table 3, entries 1-4). Similarly, the yields of aldehydes **2-3** and acyloins **4-5** dropped from 23 to 16% and from 11 to 0%, respectively. With thiazolium **17**, almost no conversion was observed indicating that a bulky group is deleterious for the activity of the catalyst (Table 3, entry 6). From these results, thiazolium iodide **11** was found the best catalyst and was selected for further optimization. The influence of the anion of a range of *N*-methyl-thiazolium salts was next investigated (Table 4). Using I, Br, CF<sub>3</sub>SO<sub>3</sub> (OTf), BF<sub>4</sub> and CF<sub>3</sub>CO<sub>2</sub> anions, the conversion of α-hydroxyketone **1** reached around 34-39% and the yields of aldehydes **2-3** and acyloins **4-5** established around 23-29% and

8-10%, respectively (Table 4, entries 1-5). Therefore, and not surprisingly, the nature of the anion has little impact on the catalytic activity as the latter arises from the corresponding *N*-methyl-thiazolylidene species. However, the conversion is much higher (52%) with thiazolium triflimide **22**, indicating that this catalyst also promotes side-reactions (Table 4, entry 6). Thiazolium benzoate **24**.PhCO<sub>2</sub>H also catalyzes the retro-benzoin condensation but afforded lower yields (Table 4, entry 7). Interestingly, the reaction also proceeds without external base showing the ability of the benzoate ion to act as an internal base for the generation of the active thiazolylidene species (Table 4, entry 8).

**Table 4.** Catalytic tests using *N*-methyl-thiazolium salts.<sup>[a]</sup>

Entry	Thiazolium salt		Conv. <sup>[b]</sup> (%)	Yield <sup>[b]</sup> (%)			
	anion			2	3	4	5
1	I	11	39	29	29	10	10
2	Br	15	36	25	23	8	8

3	CF <sub>3</sub> SO <sub>3</sub>	19	39	26	24	10	10
4	BF <sub>4</sub>	20	35	23	23	10	10
5	CF <sub>3</sub> CO <sub>2</sub>	21	34	25	25	9	9
6	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N	22	52	21	18	3	3
7	PhCO <sub>2</sub>	24.PhCO <sub>2</sub> H	30	15	14	3	3
8 <sup>[c]</sup>	PhCO <sub>2</sub>	24.PhCO <sub>2</sub> H	36	20	17	4	4

[a] Conditions: microwave tube,  $\alpha$ -hydroxyketone **1** (1:1 mixture of regioisomers, 0.2 mmol), thiazolium salts (0.04 mmol), K<sub>2</sub>CO<sub>3</sub> (0.04 mmol), dry MeCN (2 mL), 150 °C, 30 min. [b] Yields were determined by GC using n-hexadecane as internal standard. [c] No base was used in this condition.

The thermal stability of most of the precatalysts was evaluated by dynamic thermogravimetric analysis (TGA). Even if this method overestimates the thermal stability, it usually provides useful information on the short-term thermal stability of ionic liquids and is generally used for comparative purposes.<sup>[32]</sup> Moreover, contrary to imidazolium-based ionic-liquids, few TGAs were reported on thiazolium derivatives.<sup>[33]</sup> First, the influence of the alkyl chain length on the stability has been probed with a range of thiazolium iodides **11-14** and dynamic TGAs were measured under nitrogen at a heating rate of 20 °C.min<sup>-1</sup> (Figure 5). Several thermal properties including  $T_{\text{onset}}$  and  $T_{\text{peak}}$  are gathered in Table S3 in ESI.

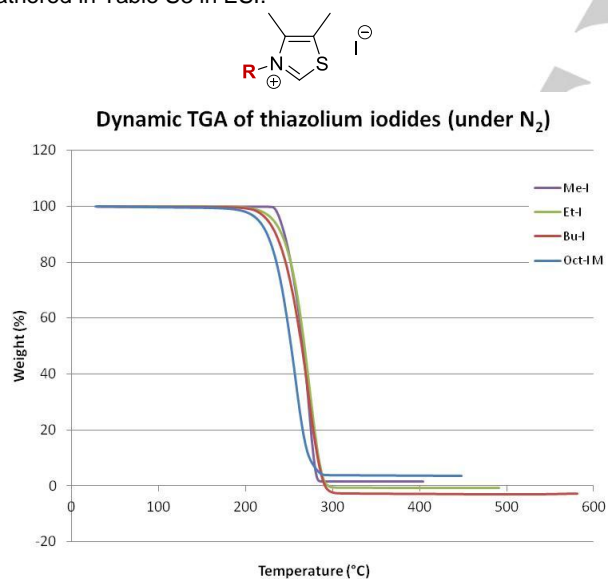


Figure 5. Dynamic TGA curves of thiazolium iodides.

The thermal stability of thiazolium salts is not significantly affected with the increase of the alkyl chain length from methyl to *n*-octyl as the dynamic TGA curves are almost superimposed. However, slight differences can be observed on the  $T_{\text{onset}}$  that is decreasing with the increase of the alkyl chain length (Table S5 in ESI). These results are in accordance with the behavior of imidazolium-based ionic liquids.<sup>[34]</sup> Then, the influence of the

anion on the thermal stability has been probed with a range of *N*-methyl-thiazolium salts (Figure 6).

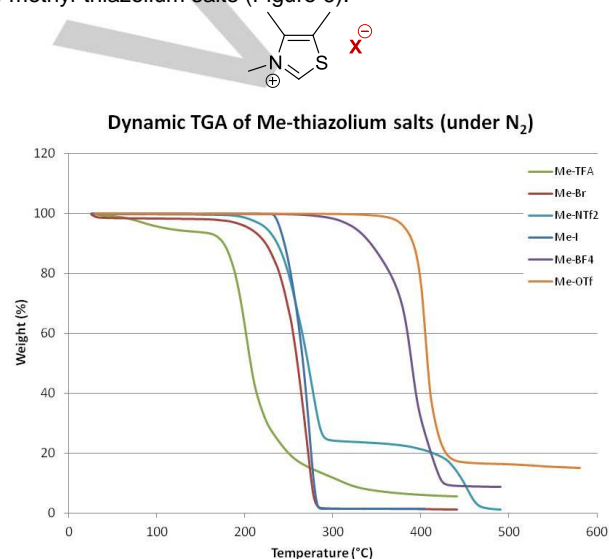


Figure 6. Dynamic TGA curves of *N*-methyl-thiazolium salts.

In this case, the thermal stability of thiazolium precatalysts is considerably affected by the nature of the anion. Halide anions such as I and Br display very similar behavior with comparable  $T_{\text{onset}}$ ,  $T_{\text{peak}}$  and  $T_{\text{endset}}$  (Table S5 in ESI). In sharp contrast, stabilized fluorinated anions present huge differences. While CF<sub>3</sub>CO<sub>2</sub> anion reduces the thermal stability compared to halides, the use of BF<sub>4</sub>, OTf and NTf<sub>2</sub> anions increases the decomposition temperature to at least 100 °C. Noteworthy, the NTf<sub>2</sub> anion, which is usually giving the best thermal stabilities in the imidazolium series, showed two degradation waves in our case. This could be probably explained by two different mode of degradation, one from the thiazolium cation and other one from the NTf<sub>2</sub> anion. These results show that the overall thermal stability of thiazolium salts is mainly governed by the nature of the anion and the relative robustness of these species could be ranked as follows: OTf > BF<sub>4</sub> > NTf<sub>2</sub> > I > Br > CF<sub>3</sub>CO<sub>2</sub>. Finally, thiazolium triflate **19** was found to be the more stable precatalyst with a degradation temperature of about 395 °C.

The cleavage of  $\alpha$ -hydroxyketone **1** under reactive distillation conditions was re-investigated using thiazolium triflate **19** that was selected as the best catalyst in terms of stability and activity (Table 5). Thus, neat  $\alpha$ -hydroxyketone **1** was heated at 180°C in the presence of thiazolium salt **19** (20 mol%) and  $K_2CO_3$  (10 mol%) and the aldehydes were simultaneously distilled under reduce pressure (1-3 mbar). Pleasingly, the distillate was recovered with an overall 75 wt% yield after only 15 minutes and the yields of aldehydes **2** and **3** were calculated to 84 and 70%, respectively (Table 5, entry 1). However, we have noticed that some of thiazolium **19** has been sublimated under these conditions. In order to prevent such inconvenience, *n*-butyl

analog **25** has been synthesized (see ESI) and used in the same reaction. Satisfyingly, aldehydes **2** and **3** were recovered with similar results and no sign of sublimation has been observed (Table 5, entry 2). Decreasing the temperature to 160°C led to similar proportions of aldehydes but the overall yield dropped to 70 wt% (Table 5, entry 3). A crude sample of  $\alpha$ -hydroxyketone **1** (83% GC purity) was also used as starting material and the aldehydes **2** and **3** were recovered with 85 and 71% yields, based on the purity of the starting material (Table 5, entry 4). These results highlight the robustness of the catalytic system developed.

**Table 5.** Cleavage of  $\alpha$ -hydroxyketone **1** under reactive distillation conditions.<sup>[a]</sup>

Entry	R	Temp. <sup>[b]</sup> (°C)	Distillate				
			m <b>2+3</b> (g)	Yield <b>2+3</b> (wt%)	GC ratio <b>2 : 3</b>	Yield <b>2</b> <sup>[c]</sup> (%)	Yield <b>3</b> <sup>[c]</sup> (%)
1	Me	180	3.00	75	61:39	84	70
2	<i>n</i> -Bu	180	3.07	75	60:40	85	71
3	<i>n</i> -Bu	160	2.82	70	60:40	80	67
4 <sup>[d]</sup>	<i>n</i> -Bu	180	2.48	75	62:38	85	71

[a] Conditions: distillation set-up,  $\alpha$ -hydroxyketone **1** (1:1 mixture of regioisomers, 4.00 g), thiazolium salt (20 mol%),  $K_2CO_3$  (10 mol%), neat, 1-3 mbar, 15 min. [b] Temperature of the oil bath. [c] Calculated yields based on calibration. [d] Crude starting material containing  $\alpha$ -hydroxyketone **1** (83%), the corresponding diketone (5%), the corresponding diol (3%) and nonanoic acid (about 6%).

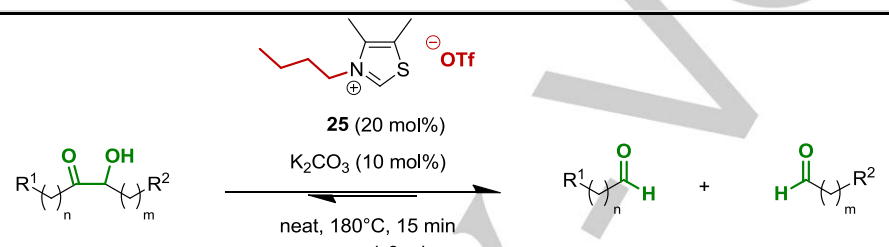
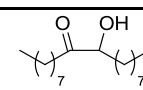

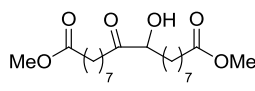
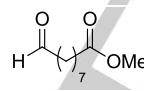
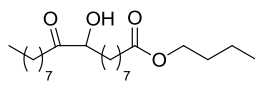

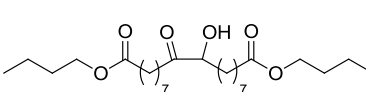
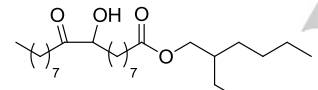

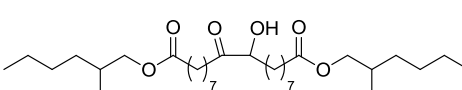
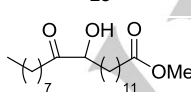

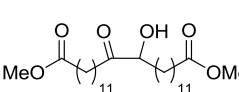
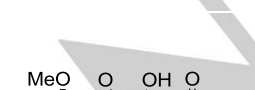
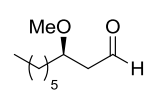
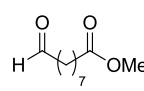
The scope of the cleavage of  $\alpha$ -hydroxyketones derived from vegetable oils has been next investigated using the previously optimized conditions (Table 6). These fatty  $\alpha$ -hydroxyketones were prepared from the corresponding diols, either by oxidation using a homogeneous palladium-neocuproine complex or by dehydrogenation using a heterogeneous ruthenium catalyst.<sup>[10a]</sup> Symmetrical  $\alpha$ -hydroxyketones **4** and **5**, derived from self-metathesis products of methyl oleate,<sup>[35]</sup> gave nonanal **2** and methyl azelaaldehyde **3** with 88 and 80% isolated yields, respectively (Table 6, entries 1-2). This protocol was also applied to other fatty acid derivatives. Unsymmetrical  $\alpha$ -hydroxyketones **26** and **28** derived from butyl and 2-ethylhexyl oleate gave nonanal **2** with 82 and 93% yield, respectively (Table 6, entries 3-4). In these cases, the remaining bifunctional aldehydes could not be distilled due to their high boiling point and undergo NHC-catalysed self-benzoin condensation.

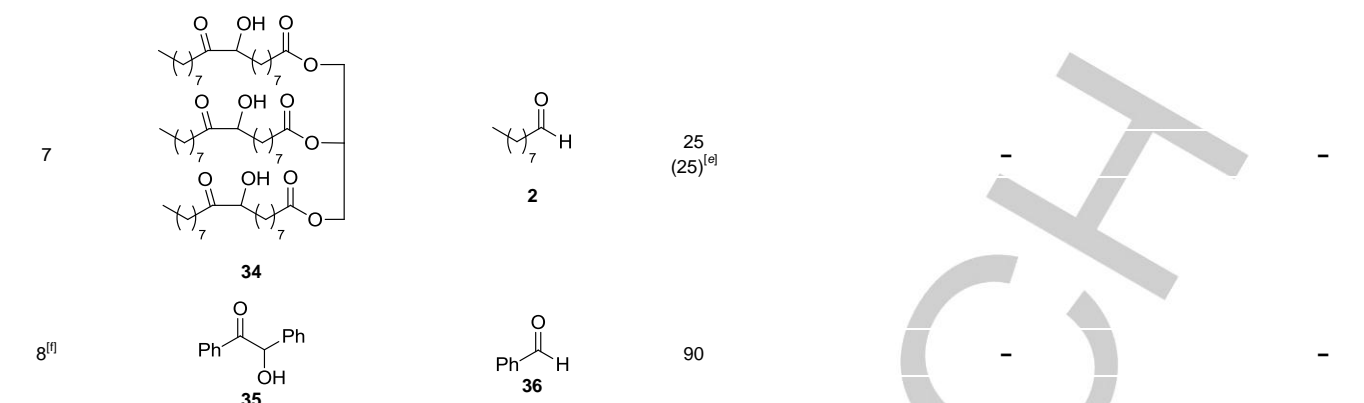
Consequently, symmetrical acyloins **27** and **29** were isolated from the residue by column chromatography and were obtained with 39 and 54% yields, respectively. Similarly,  $\alpha$ -hydroxyketone **30** derived from methyl erucate gave nonanal **2** with an excellent 98% yield and symmetrical acyloin **31** was isolated from the residue with 30% yield (Table 6, entry 5). The  $\alpha$ -hydroxyketone **32** derived from methyl ricinoleate was next cleaved to give (*R*)-3-methoxynonanal **33** and aldehyde **3** but only poor yields were obtained (Table 6, entry 6). We hypothesized that the methoxy group was bulky enough to prevent the addition of the *N*-butyl catalyst **25** onto the carbonyl group. For that reason, the reaction was repeated with *N*-methyl catalyst **19**. Satisfyingly, the yields of aldehydes **33** and **3** improved to 15 and 30%, respectively (Table 6, entry 6, results in brackets). However, these results are not as good as those obtained previously. In fact, due to the presence of the methoxy group, the starting

material **32** exists as a mixture of four inseparable isomers (NMR ratio = 25:18:21:36), *i.e.* two diastereoisomers for each regioisomer. It is likely that one of these species reacts faster than the others with catalyst **19** to give the cleavage compounds, thus leading to some regio- or diastereoselection. This could also explain why some starting material was recovered from the residue. Tris( $\alpha$ -hydroxyketone) **34**, prepared from high-oleic sunflower oil (85% oleic acid content) and containing about 60% of  $\alpha$ -hydroxyketone functionality, was also subjected to the cleavage conditions (Table 6, entry 7). Remarkably, nonanal **2** was obtained with 25% yield (25% with thiazolium **19**) indicating that challenging substrates such as triglycerides could be also

cleaved under the current conditions. This opens the possibility to valorize waste vegetable oils to value-added aldehydes, that could be used as such or for the preparation of bio-based surfactants. Moreover, bifunctional aldehydes and symmetrical acyloins obtained through this methodology could be also used as building-blocks for the preparation of bio-based polyesters and polyamides. Finally, to further demonstrate the interest of this methodology, benzoin **35** was cleaved under reactive distillation conditions (Table 6, entry 8). Satisfyingly, benzaldehyde **36** was obtained with 90% isolated yield, thus showing the versatility of the method developed.

**Table 6.** Scope of  $\alpha$ -hydroxyketones derived from vegetable oils.<sup>[a]</sup>

				
Entry	$\alpha$ -hydroxyketones	Yields <sup>[b]</sup> (%) of cleavage compounds in distillate		Yields <sup>[c]</sup> (%) of the main product in the residue
1 <sup>[d]</sup>			88	–
2			80	–
3			82	 39
4			93	 54
5			98	 30
6			6 <sup>[c]</sup> (15) <sup>[c,e]</sup>	mainly starting material
			9 <sup>[c]</sup> (30) <sup>[c,e]</sup>	–



[a] Conditions: distillation set-up,  $\alpha$ -hydroxyketone (1:1 mixture of regioisomers), thiazolium salt (20 mol%),  $K_2CO_3$  (10 mol%), neat, 180°C (oil bath temperature), vacuum = 1–3 mbar, 15 min. [b] Isolated yields. [c] Isolated yields after purification by column chromatography. [d] The vacuum pressure was set at 10 mbar to avoid the distillation of the starting material. [e] Yield in brackets was obtained using catalyst **19**. [f] The vacuum pressure was set at 50 mbar.

## Conclusions

In conclusion, we have developed a robust catalytic system based on thiazolium salts for the cleavage of the  $\alpha$ -hydroxyketone derived from methyl oleate. The reaction proceeds through a retro-benzoin process under reactive distillation conditions. The cleavage products, namely, nonanal and methyl azelaaldehyde, were obtained with 85 and 70% yields, respectively. A range of  $\alpha$ -hydroxyketones derived from several fatty acids has been also cleaved to give the corresponding bio-based aldehydes with up to 98% isolated yields. Finally, this protocol was also found applicable to a high-oleic sunflower oil derivative, opening the possibility to valorize waste vegetable oils. The aldehydes produced through this methodology are excellent platforms for the preparation of bio-based surfactants or building-blocks for polymer applications.

## Experimental Section

**General procedure for the thiazolylidene-catalysed cleavage of  $\alpha$ -hydroxyketone under microwave conditions:** In a 5-mL microwave tube, 9(10)-hydroxy-10(9)-oxooctadecanoate **1** (1:1 mixture of regioisomers) (65.7 mg, 0.2 mmol, 1 equiv), the thiazolium salt (0.04 mmol, 20 mol%) and  $K_2CO_3$  (5.5 mg, 0.04 mmol, 20 mol%) were added. The tube was flushed with argon and dry  $CH_3CN$  (2 mL) was added. The mixture was stirred under microwave irradiation at the desired temperature for a period of time. The mixture was cooled down to room temperature and analyzed by GC using hexadecane as internal standard.

**Typical procedure for the thiazolylidene-catalysed cleavage of  $\alpha$ -hydroxyketone to aldehydes by reactive distillation:** In a 25-mL bottom flask, under an argon atmosphere,  $K_2CO_3$  (1.2 mmol, 165.8 mg, 10 mol%), 3-butyl-4,5-dimethylthiazol-

3-ium triflate **25** (766.5 mg, 2.4 mmol, 20 mol%) and  $\alpha$ -hydroxyketone (12 mmol) were added and the distillation set-up was installed. Then, the mixture was heated at 180°C (oil bath pre-heated at 180°C) under reduced pressure (vacuum = 1–3 mbar, except for the case of  $\alpha$ -hydroxyketones **4** and **35**). The distillate was collected, weighted and analysed by GC, using *n*-hexadecane as internal standard. The residue was also weighted and analyzed by GC and NMR. If needed, the aldehydes could be further purified by flash chromatography (cyclohexane/EtOAc 99.8:0.2  $\rightarrow$  95:5).

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**Keywords:** Vegetable oils • Thiazolium salts •  $\alpha$ -hydroxyketones • Retro-benzoin condensation • Aldehydes

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